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TI - MANUFACTURE OF SURFACE TREATED ARTICLE
IN - BESSHO TOMOYUKI;YUASA MOTOKAZU
PA - SEKISUI CHEMICAL CO LTD
IC - C23C16/515 ; C08J7/00 ; C23C16/505 ; C08L101/00

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TI - Surface treating e.g. antistatic film, involves introducing gas between substrates and contacting with counter electrodes or solid dielectric between electrodes
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PA - (SEKI) SEKISUI CHEM IND CO LTD
IC - C08J7/00 ;C08L101/00 ;C23C16/505 ;C23C16/515
AB - JP2000212753 NOVELTY - Gas for process (90,91) is introduced continuously between two sheet-like base materials (12,13) and base materials are contacted with counter electrodes (30,40 and 31,41) or solid dielectric (60-63) which respectively and mutually oppose each other, between counter electrodes.
- DETAILED DESCRIPTION - Electric field is impressed between counter electrodes at atmospheric pressure, thereby discharge plasma is generated and plasma treatment of base materials is carried out and plasma treated base material is provided as surface treated goods (14,15).
- USE - For manufacturing various functional films such as anti-reflecting coating membrane, optical permselective membrane, infrared ray reflecting film, antistatic film, electromagnetic wave seal film and semiconductor device material.
- ADVANTAGE - The surface treated good which excels in adhesion of thin film and base material is manufactured easily, efficiently and inexpensively. The formation of sediment on the material during the plasma treatment is eliminated. The need of large-sized exhaust gas device for the process is eliminated. The feeding and taking out of raw material and the product from the apparatus becomes easier.
- DESCRIPTION OF DRAWING(S) - The figure shows apparatus for manufacturing surface treated goods.

- Sheet-like base materials 12,13
- Surface treated goods 14,15
- Counter electrodes 30,40 and 31,41
- Solid dielectric 60-63
- Gas for process 90,91
- (Dwg.3/4)

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TI - MANUFACTURE OF SURFACE TREATED ARTICLE

AB - PROBLEM TO BE SOLVED: To provide a manufacturing method of a surface-treated article in which the surface-treated article excellent in adhesivity of a thin film to a substrate can be efficiently under the pressure in the vicinity of the atmospheric pressure without any excessive investment on facilities, and deposited substances by the plasma processing are small in quantity.

- SOLUTION: In a manufacturing method of surface treated articles 14, 15, processing gases 90, 91 are introduced at the pressure close to the atmospheric pressure between electrodes30/40 and 31/41 opposite to each other in which solid dielectric materials 60-63 are installed on at least one set of surfaces opposite to each other, the discharge plasma is generated by applying the pulsed electric field to the electrodes 30/40 and 31/41 opposite to each other, and substrates 12, 13 provided between the electrodes 30/40 and 31/41 opposite to each other are plasma-processed. Two substrates 12, 13 are closely attached to the electrodes 30/40 and 31/41 opposite to each other or the solid dielectric materials 60-63, and the processing gases 90, 91 are continuously introduced between two substrates12, 13.

SI - C08L101/00

I - C23C16/515 ;C08J7/00 ;C23C16/505

* NOTICES * JP 2000-212753

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the manufacture method of a surface treatment article.
[0002]
[Description of the Prior Art] Although the base material which consists of plastics, a metal, paper, fiber, etc. is widely used as home use and an industrial use material, if specific functions, such as an electrical property, an optical property, and a mechanical characteristic, are given to the front face, the use is expanded further and it comes to have big added value.
[0003] As a method of manufacturing the surface treatment article which comes to carry out the laminating of the thin film which gave the specific function to the front face of the above base materials, a vacuum deposition method, the sputtering method, the ion beam method, the ion plating method, the plasma CVD method using the glow discharge under reduced pressure, etc. are learned. However, each of these methods is performed by the vacuum system, large-scale facilities, such as a vacuum chamber and a large-sized vacuum pump, are required for them, and there are various kinds of limitations in manufacture.
[0004] In order to form a thin film in the front face of a long base material by the vacuum system, two kinds, a batch method and a continuous method, are in manufacture. In a batch method, thin film formation is performed by reduced pressure and the closed system, the roll which wound the base material around the long picture is put into a vacuum chamber, and a thin film is formed by the front face, beginning to roll a base material from a roll in this. By this method, vacuous release and vacuous formation must be repeated for every carrying in of a raw material or taking out of a product, and with the size of a facility, since a limitation appears in the capacity of the diameter of a base-material roll, a thin film raw material, etc., productive efficiency also becomes bad.
[0005] In a continuous method, in order to acquire a reduced pressure state, a differential-pumping method is used, and it exhausts gradually down to reduced pressure from atmospheric pressure, and a thin film is formed all over the space which held continuously the degree of vacuum required for membrane formation of a thin film. Although this method is easy for carrying in and a raw material supplement of a roll base material, since it is necessary to exhaust beyond the inflow of the air into a thin film deposition system, and to hold a degree of vacuum, a mass vacuum pump is needed and growing gigantic of a facility is not avoided.
[0006] Moreover, when giving two or more functions to one base material or adding a more advanced function, the attempt which carries out the laminating of two or more sorts of thin films is made. However, when forming a multilayer industrially, in order to have to repeat the cycle of release of the membrane formation-vacuum of a vacuous formation-thin film for every kind of layer in a batch method, it is very inefficient and is not realistic. Moreover, in a continuous method, a large-scale facility is required also of a monolayer, and introduction of the process of multilayer formation is difficult. Furthermore, correspondence of a little variety was difficult for the continuous method on plant-and-equipment investment, and the correspondence to the use which adds a specific function to a base material separately etc. was very difficult.
[0007] A proposal various in the method of manufacturing the above surface treatment articles is made. in JP,2-181701,A and a ****** No. 518202 [three to] official report Although the method of

controlling the degree of incident angle of an electron gun and the angle of a vacuum evaporationo roll and the source of vacuum evaporationo, and forming a cascade screen on the surface of a base material in a vacuum deposition method is proposed The batch method had to be adopted having consented to the very inefficient thing, since plant-and-equipment investment became excessive too much for carrying out by there being no change in the continuous method using the differential-pumping method.

[0008]

[Problem(s) to be Solved by the Invention] Then, while this invention persons generate electric discharge plasma by introducing the gas for processing between the counterelectrodes by which the solid dielectric was installed in one [at least] opposite side, and impressing the electric field pulse-ized between the pressure near the atmospheric pressure, nothing, and the counterelectrode, the manufacture method of the surface treatment article which carries out plasma treatment of the base material prepared between the aforementioned counterelectrodes is proposed (Japanese-Patent-Application-No. 10-No. 45393 specification). However, in the above-mentioned method, the base material was prepared on one electrode and its productive efficiency was inadequate. Moreover, the sediment by plasma treatment adhered to the electrode side in which the base material is not prepared, and the electrode needed to be cleaned to whenever [the].

[0009] the technical problem of the above [this invention] -- solving -- the bottom of the pressure near the atmospheric pressure -- and it aims at offering the manufacture method of a surface treatment article that do not need excessive plant-and-equipment investment, but manufacture efficiently the surface treatment article excellent in the adhesion of a thin film and a base material, and there are few sediments by plasma treatment and they end

[0010]

[Means for Solving the Problem] The manufacture method (henceforth a "this invention") of a surface treatment article according to claim 1 While generating electric discharge plasma by introducing the gas for processing between the counterelectrodes by which the solid dielectric was installed in one [at least] opposite side, and impressing the electric field pulse-ized between the pressure near the atmospheric pressure, nothing, and the counterelectrode It is the manufacture method of the surface treatment article which carries out plasma treatment of the base material prepared between the aforementioned counterelectrodes, and the base material of two sheets is stuck to the counterelectrode or solid dielectric which confronted each other, respectively, and the gas for processing is continued and introduced between the base materials of two sheets.

[0011] In this invention, the bottom of the pressure near the atmospheric pressure means the bottom of the pressure of 13.3-106.4kPa, pressure regulation is easy, and the range of 93.1-103.74kPa to which equipment becomes simple is desirable.

[0012] Under the pressure near the atmospheric pressure, shifting to an arc discharge state in an instant is known except specific gas, such as helium and a ketone, without holding the stable plasma electric discharge state. However, if the pulse-ized electric field are impressed, before shifting to arc discharge, electric discharge can be stopped, and it realizes, and the cycle of starting electric discharge again can be stabilized and can generate electric discharge plasma.

[0013] According to the method of impressing the pulse-ized electric field in this invention, it is possible to generate electric discharge plasma regardless of the kind of gas which exists all over plasma generating space. Although it was indispensable to have performed processing using electric discharge plasma also under well-known low voltage conditions conventionally within the airtight container intercepted from the open air under a specific gas atmosphere, according to this invention, an open system or the low airtight system of the grade which prevents a free gaseous spill can also be carried out, and the high-density plasma state can be realized.

[0014] In this invention, the build up time of field strength of the electric field to impress is desirable inkV [1-100 //cm] 100 or less microseconds. By impressing the pulse electric field which have a steep standup, the gas molecule which exists all over plasma generating space is because it excites efficiently. It is difficult to ionize efficiently the molecule which excites to level with the higher molecule already ionized when excitation of a molecule small [of the molecule which is equivalent to supplying gradually the energy which has the size from which impressing pulse electric field with a late standup differs, and is first ionized by low energy i.e., the first ionization potential,] takes

place preferentially and energy high next is supplied, and exists all over plasma generating space. On the other hand, according to the pulse electric field whose build up time is 100 or less microseconds, it is equivalent to giving energy to the molecule which exists all over space all at once, the absolute number of the molecule in the state where it ionized in space increases, and plasma density becomes a bird clapper highly. It can do and the high-density plasma state can be realized.

[0015] In this invention, processing takes time too much as the field strength of the electric field to impress is less than 1 kV/cm, and if 100 kV/cm is exceeded, it will become easy to generate arc discharge. In addition, the above-mentioned field strength says what **(ed) the value of the peak-peak of not an effective voltage but the voltage impressed to inter-electrode in inter-electrode distance.

[0016] When it installs a solid dielectric in one side of the above-mentioned electrode, the part which electric discharge plasma generates is the space between solid dielectrics between a solid dielectric and an electrode, when a solid dielectric is installed in the both sides of the above-mentioned electrode.

[0017] As an electrode, what consists of alloys, such as metal simple substances, such as copper and aluminum, stainless steel, and brass, an intermetallic compound, etc. is mentioned, for example. In order to avoid generating of the arc discharge by electric-field concentration; as for a counterelectrode, it is desirable that it is the structure where the distance between counterelectrodes serves as abbreviation regularity. As electrode structure of fulfilling this condition, an parallel monotonous type, a hyperboloid opposite monotonous type, coaxial-circles telescopic structure, etc. are mentioned. Since there is a possibility that arc discharge may occur at the end that an electrode edge is sharp, as for an edge, it is desirable to have carried out taper processing.

[0018] As a solid dielectric, it installs in one side or the both sides of an opposite side of an electrode. Under the present circumstances, a solid dielectric and the electrode of the side installed stick, and are wearing the opposite side of the touching electrode completely. If there is a part which electrodes counter directly, without being covered by the solid dielectric, arc discharge will arise from there.

[0019] As a solid dielectric, multiple oxides, such as metallic oxides, such as plastics, such as a polytetrafluoroethylene and a polyethylene terephthalate, glass, a silicon dioxide, an aluminum oxide, a zirconium dioxide, and a titanium dioxide, and a barium titanate, etc. are mentioned, for example.

[0020] Although the shape of the shape of a sheet and a film has as the configuration of a solid dielectric, it is desirable that thickness is 0.05-4mm. The high voltage is taken to generate electric discharge plasma, if too thick, if too thin, dielectric breakdown will happen at the time of voltage impression, and arc discharge will occur.

[0021] Moreover, as for a solid dielectric, it is desirable that specific inductive capacity is two (bottom of the 25 degreeC environment, following **) or more. Specific inductive capacity can mention a polytetrafluoroethylene, glass, the film that consists of a metallic oxide as an example of two or more dielectrics, for example. Furthermore, in order to be stabilized and to generate high-density electric discharge plasma, it is desirable that specific inductive capacity uses ten or more fixed dielectrics. Although especially the upper limit of specific inductive capacity is not limited, about 18,500 thing is known for an actual material. It is desirable for specific inductive capacity to consist of a metallic-oxide thin film mixed with 5 - 50 % of the weight of oxidization titanium and 50 - 95 % of the weight of aluminum oxides or a metallic-oxide thin film containing a zirconium oxide as ten or more solid dielectrics, and to use that whose thickness of the thin film is 10-1000 micrometers.

[0022] Although an inter-electrode distance is determined in consideration of the purpose using the thickness of a solid dielectric, the size of applied voltage, and plasma etc., it is desirable that it is 1-50mm. In less than 1mm, if it is difficult for an inter-electrode distance to be too small and to prepare a base material on each electrode and it exceeds 50mm, it will become difficult to generate uniform glow discharge plasma.

[0023] Moreover, in this invention, by passing a base material in succession between the counterelectrodes which adjoined two or more sets and were prepared, a thin film of the same kind or of a different kind makes it deposit continuously one by one, and can manufacture a surface

treatment article for each class. In this case, two or more sets of counterelectrodes adjoin, and are arranged, and it is carried out in the equipment with which the solid dielectric is installed in one [at least] opposite side of this counterelectrode. Therefore, the electric discharge plasma treatment equipment of each smallness unit of this invention does not need to have the same arrangement of the solid dielectric of all counterelectrodes, if the above-mentioned conditions are satisfied.

[0024] In this case, the field where the counterelectrode of each class is contained constitutes the electric discharge plasma treatment equipment of the small unit which became independent, respectively, it is supplied so that the gas for processing may serve as a pressure near the atmospheric pressure at this equipment, and by the well-known method, a base material is run the space between counterelectrodes continuously, and is introduced into the electric discharge plasma treatment equipment of the following small unit one by one.

[0025] The example of a pulse-voltage wave is shown in drawing 1 . A wave (A) and (B) are [a square wave type and the wave (D) of an impulse type and a wave (C)] become [irregular] type waves. Although voltage impression mentioned what is the repeat of positive/negative to drawing 1 , you may use the so-called wave of the piece sinuate which impresses voltage to a positive or negative polarity [one of] side.

[0026] Although the pulse-voltage wave in this invention is not limited to the wave mentioned here, ionization of the gas in the case of plasma generating is efficiently performed, so that the build up time of a pulse is short. When the build up time of a pulse exceeds 100 microseconds, an electric discharge state will become being easy to shift to an arc unstable, and it will become impossible to expect the high-density plasma state by pulse electric field. Moreover, although the quicker one of build up time is good, it is difficult for the equipment which has the field strength of the size which is the grade which plasma generates in an ordinary pressure, and is made to generate electric field with quick build up time to have restrictions, and to realize the pulse electric field of the build up time for less than 40ns actually. 50ns - 5 microseconds of build up time are more desirable. In addition, build up time here means time for voltage change to be positive continuously.

[0027] Moreover, the falling time of pulse electric field also has a steep desirable thing, and it is desirable that it is the same time scale for 100 or less microseconds as build up time. Although it changes also with pulse electric-field generating technology, by the power unit used in the example of this invention, it falls with build up time and time can set it as the same time, for example.

[0028] Furthermore, you may become irregular using pulse shape, build up time, and the pulse from which frequency differs. Moreover, in impression of a pulse voltage, you may superimpose a direct current.

[0029] As a power supply used for impression of such a pulse voltage, the thing of a publication is used [Japanese Patent Application No. / No. 186314 / nine to] /, for example.

[0030] Setting to the electric discharge obtained by the above-mentioned method, the discharge current density between counterelectrodes is 0.2 - 300 mA/cm2. Being made is desirable.

[0031] As for the pulse-ized electric field, in this invention, it is desirable that 0.5-100kHz and pulse duration are made for frequency with 1 - 1000 microseconds.

[0032] Since plasma density is low, the frequency of pulse electric field requires time for processing too much, as it is less than 0.5kHz, and if it exceeds 100kHz, arc discharge will become easy to generate it. More preferably, it is 1kHz or more and processing speed can be greatly raised by impressing the pulse electric field of such high frequency.

[0033] Moreover, the pulse duration in the above-mentioned pulse electric field will become easy to shift to arc discharge, if electric discharge becomes being less than 1 microsecond with an unstable thing and it exceeds 1000 microseconds. It is 3 microseconds - 200 microseconds more preferably. Here, although one pulse duration has shown the example in drawing 2 , it means the time in the pulse electric field which consist of a repeat of ON and OFF for a pulse to continue. By intermittence type pulse like drawing 2 (a), although pulse duration is equal to pulse width time, unlike pulse width time, in the pulse of a wave like drawing 2 (b), time including two or more of a series of pulses is said.

[0034] Furthermore, in order to stabilize electric discharge, it is desirable to have the OFF time continued for at least 1 microsecond in 1ms of charging time values. When the above-mentioned discharge current density means the value which **(ed) current value which flows to inter-electrode

by electric discharge in the area of the direction which intersects perpendicularly with the flow direction of the current in discharge space and an parallel monotonous type thing is used as an electrode, it is equivalent to the value which **(ed) the above-mentioned current value in the opposite area. Although pulse-like current flows in this invention in order to form pulse electric field in inter-electrode, the value which **(ed) the maximum of the pulse current, i.e., peak to peak value, in the above-mentioned area in this case is said.

[0035] 0.2 which it is shown clearly by research of this invention persons that it is the value to which discharge current density influences manufacture of a surface treatment article reflecting plasma density, and described above inter-electrode discharge current density in the glow discharge under the pressure near the atmospheric pressure as shown below - 300 mA/cm2 By considering as the range, uniform electric discharge plasma is generated and the manufacture result of a good surface treatment article can be obtained.

[0036] As a base material used for this invention, plastics, such as polyethylene, polypropylene, polystyrene, a polycarbonate, a polyethylene terephthalate, a polyphenylene ape fight, a polyether ether ketone, a polytetrafluoroethylene, and acrylic resin, glass, a ceramic, a metal, etc. are mentioned, for example. Especially as a configuration of a base material, although not limited, in processing continuously, it is suitable for long picture type base materials, such as the shape of the shape of a tabular and a film, and a pipe.

[0037] Although the above-mentioned base material may be fixed and prepared in an electrode or a solid dielectric by the batch type, it is desirable on productive efficiency to make it run an electrode top continuously.

[0038] In this invention, the laminating of arbitrary thin films is possible by selection of the gas (it is hereafter called the gas for processing) which exists not only in the metallic element content gas mentioned later but in electric discharge plasma generating space.

[0039] As gas for processing, by using fluorine content compound gas, a fluorine content machine can be made to be able to form in a base-material front face, surface energy can be made low, and a water-repellent front face can be obtained.

[0040] Especially as a fluorine element content compound, although not limited, it is desirable to use fluorine-carbon compounds which do not generate the hydrogen fluoride which is harmful gas, such as 8 6 fluoride [propylene] (CF3CFCF2), cyclobutane, etc. fluoride (C4F8), from a viewpoint on safe.

[0041] Moreover, a hydrophilic polymerization film can also be made to deposit in a molecule by processing under the atmosphere of the monomer which has a hydrophilic radical and a polymerization nature unsaturated bond. As the above-mentioned hydrophilic radical, hydrophilic radicals, such as a hydroxyl group, a sulfonic group, a sulfonate machine, the 1st class, the 2nd class or the 3rd class amino group, an amide group, a quarternary-ammonium-salt machine, a carboxylic-acid machine, and a carboxylate machine, etc. are mentioned. Moreover, even if it uses the monomer which has a polyethylene-glycol chain, a hydrophilic polymerization film can be deposited similarly.

[0042] As the above-mentioned monomer, acrylic-acid, methacrylic-acid, acrylamide, methacrylamide, N, and N-dimethyl acrylamide, acrylic-acid sodium, methacrylic-acid sodium, an acrylic-acid potassium, a methacrylic-acid potassium, styrene sulfonic-acid sodium, allyl alcohol, an allylamine, polyethylene-glycol dimethacrylate ester, polyethylene-glycol diacylic ester, etc. are mentioned, and these at least one sort can be used.

[0043] If the gas for processing introduced in this invention uses the thing containing metallic element content gas, the surface treatment article with which the oxide film of the used metallic element was formed in the base-material front face can be obtained.

[0044] An electric discharge state cannot be easily stabilized by the atmosphere containing such metallic element content gas, and unless it is based on the method using the electric field by which this invention was pulse-ized, it cannot process. As the above-mentioned metal, for example aluminum, As, Au, B, Bi, Sb, calcium, Cd, Cr, Co, Cu, Fe, Ga, germanium, Hg, Hf, In, Ir, Li, Mg, Mn, Mo, Na, nickel, P, Pb, Po, Pt, Rh, Metals, such as Se, Si, Sn, Ta, Te, Ti, V, W, Y, Zn, and Zr, are mentioned, and the gas for processing, such as a metal organic compound, a metal-halogenated compound, metal-hydride, a metal-halogenated compound, and a metal alkoxide, is mentioned as gas

containing this metal.
[0045] When it specifically explains taking the case of the case where a metal is Si, a tetramethylsilane [Si (CH3)4], Organometallic compound;4 silicon fluorides, such as dimethylsilane [Si(CH3)2H2] and a tetraethyl silane [Si (C2H5)4] (SiF4), Metal halogenated compounds, such as four silicon chlorides (SiCl4) and two silicon chlorides (SiH2Cl2); A mono silane (SiH4), Metal hydride, such as a disilane (SiH3SiH3) and trishiran (SiH3SiH2SiH3); A tetramethoxy silane [Si (OCH3)4], Metal alkoxides, such as a tetrapod ethoxy silane [Si (OC2H5)4], etc. are mentioned, and these at least one sort including other metals can be used if needed. In the above-mentioned metal content gas, in consideration of safety, what does not have danger, such as ignition and explosion, in the ordinary temperature of a metal alkoxide metallurgy group halogenated compound etc. and the atmosphere is desirable, and a metal alkoxide is suitably used from the point of generating of corrosive and harmful gas.
[0046] What is necessary is just to introduce into discharge space through a vaporizer, if it has the shape of a liquid and a solid-state, although it can introduce into discharge space as it is, if the above-mentioned metal content gas is a gas.
[0047] It is more desirable than an atmosphere gas independent [the viewpoint of economical efficiency and safety to / above-mentioned / for processing] to process in the atmosphere thinned with dilution gas. As dilution gas, rare gas, such as helium, neon, an argon, and a xenon, nitrogen gas, etc. are mentioned, and these at least one sort is used, for example. Moreover, when using dilution gas, as for the rate of the gas for processing, it is desirable that it is 0.01 to 10 volume %.
[0048] In addition, it is advantageous, when the way of the compound which has many electrons as a controlled atmosphere (gas for processing) raises plasma density and high-speed processing is performed, as mentioned above. However, an argon or nitrogen is easy to receive and suitable at a cheap point.
[0049] In this invention, the gas for processing is continued and introduced between the base materials of two sheets prepared by sticking the gas for processing on a counterelectrode or a solid dielectric between the above-mentioned counterelectrodes. In this case, a gas supply machine is formed so that the gas for processing may be introduced between the base materials of two sheets, and the gas for processing is continuously introduced towards a base material from this gas supply machine.
[0050] As for the above-mentioned base material, it is desirable to make it run an electrode top continuously as mentioned above. In case it is made to run continuously, the kind of gas for processing introduced into the opposite above-mentioned continuation target should just supply gas of the same kind continuously from a gas supply machine to form one kind of thin film in a base material, and it should just supply the gas of another kind from two sets of gas supply machines to form the thin film of two or more kinds.
[0051] The method of introducing the gas for processing introduced between counterelectrodes in this invention by the well-known method, for example, blowing off the gas for processing with the gas supply vessel of the shape of a slit or a nozzle, the method of preparing the hole which supplies the gas for processing towards the request to the electrode which counters a base-material processing side, and blowing off this, a pump, a blower, and a blower are used, and the method of supplying and circulating etc. is mentioned to inter-electrode.
[0052] In this invention, it is also desirable to improvement in the adhesion of a base material, a thin film, or thin films to carry out plasma treatment to the field where the laminating of a base material or at least one sort of thin films was carried out beforehand.
[0053] Although the atmosphere at the time of carrying out plasma treatment beforehand will not be limited especially if the above-mentioned base material and a thin film are not degraded remarkably, from a viewpoint of economical efficiency and safety, rare gas, such as helium, neon, an argon, and a xenon, nitrogen gas, etc. are mentioned, and these at least one sort is used, for example.
[0054] Since a process is not stabilized in order that electric discharge may arc-ize, if too high [when the applied voltage at the time of carrying out plasma treatment beforehand is too low, it has little improvement in the adhesion of a base material, a thin film, or thin films, and], in argon atmosphere, 1-2kV is 1.2-1.7kV desirable still more preferably, and 6-11kV is 7-8.5kV desirable still more preferably in nitrogen atmosphere.

[0055] Moreover, since plasma density will become high, a base material or a thin film will be deleted flat and smooth, if too high [when the frequency at the time of carrying out plasma treatment is too low, it has little improvement in the adhesion of a base material, a thin film, or thin films, and] and improvement in the adhesion of a base material, a thin film, or thin films decreases, in argon atmosphere or nitrogen atmosphere, 1-8kHz is 2-4kHz desirable still more preferably.
[0056] Furthermore, when it is too short, it has little improvement in the adhesion of a base material, a thin film, or thin films, and if too long, since a base material or a thin film is deleted flat and smooth and the improvement of required for plasma treatment time in the adhesion of a base material, a thin film, or thin films will decrease, in argon atmosphere or nitrogen atmosphere, 5-20sec is desirable [time].
[0057] (Operation) By the manufacture method of the surface treatment article of this invention introducing the gas for processing between the counterelectrodes by which the solid dielectric was installed in one [at least] opposite side, and impressing the electric field pulse-ized between the pressure near the atmospheric pressure, nothing, and the counterelectrode While generating electric discharge plasma, it is the manufacture method of the surface treatment article which carries out plasma treatment of the base material prepared between the aforementioned counterelectrodes. In the state where stuck the base material of two sheets to the counterelectrode or solid dielectric which confronted each other, respectively, the gas for processing was introduced between counterelectrodes since the gas for processing is continued and introduced between the base materials of two sheets, and it was made with the pressure near the atmospheric pressure The pulse-ized electric field are impressed, by impressing predetermined pulse electric field to a counterelectrode, the electric discharge plasma depending on the aforementioned gas for processing occurs, and a thin film is formed in the base material of two sheets prepared into this electric discharge plasma at the same time it generates the stable high-density plasma.
[0058] Moreover, since plasma treatment can be performed by the ordinary pressure, processing is performed under the pressure near the atmospheric pressure in equipment. The large-scale exhaust like [that it should just change the seal of the inlet of a base material and the exhaust port into the secret state of a grade where the leakage of a gas can be permitted] the processing performed by the vacuum system is not needed. Therefore, supply of a base material, change of a base material, and change of gas composition can be performed freely, and can manufacture various kinds of surface treatment articles economically.
[0059] Furthermore, a thin film can be formed between short time, without arc discharge occurring, while the gas molecule which exists all over plasma generating space when the voltage build up time of the electric field pulse-ized [above] takes and field strength takes 100 or less microseconds for 1 - 100 kV/cm excites efficiently.
[0060]
[Embodiments of the Invention] The form of the operation of this invention to the following is explained in detail, referring to a drawing. Drawing 3 is the ** type view showing an example of the equipment used for the manufacture method of the surface treatment article of this invention. As shown in drawing 3 , the equipment used for this invention It mainly consists of the high-voltage pulse power supply sections 10 and 11, electric discharge plasma treatment equipments 20 and 21, **** rolls 80 and 81, and taking over rolls 82 and 83. Each electric discharge plasma treatment equipments 20 and 21 consist of an parallel monotonous type counterelectrode (the up electrodes 30 and 31, lower electrodes 40 and 41), the gas supply sections 50 and 51 for processing, solid dielectrics 60, 61, 62, and 63, and the gas discharge sections 70 and 71 for processing.
[0061] Moreover, the up electrodes 30 and 31 are equipped with 60 and 61, and, as for the solid dielectric, the lower electrodes 40 and 41 are equipped with 62 and 63.
[0062] Various kinds of gas 90 and 91 for processing between the counterelectrodes (namely, 30/40, 31/41) of the electric discharge plasma treatment equipments 20 and 21 under the pressure near the atmospheric pressure Arbitrary kinds are chosen and introduced according to the purpose, and the pulse-ized electric field by above-mentioned conditions are impressed to each electrode. The electric discharge plasma according to the kind of gas for processing is generated. to this at the solid dielectrics 60 and 61 of the up electrodes 30 and 31 a base material 12 A base material 13 is stuck to the solid dielectrics 62 and 63 of the lower electrodes 40 and 41, respectively, and various kinds of

thin films accumulate on the undersurface of a base material 12, and the upper surface of a base material 13, respectively.
[0063] As described above, the kind of gas 90 and 91 for processing introduced into each electric discharge plasma treatment equipments 20 and 21 changes with purposes, and even if, and it is different species, it is not cared about.
[0064] Heating and cooling systems 84 and 85 are adjacently formed in each electric discharge plasma treatment equipments 20 and 21, and base materials 12 and 13 have come be made to desired temperature. Of course, heating and a cooler style are included in the electric discharge plasma treatment equipments 20 and 21, and it does not matter as a temperature control being possible.
[0065] The seal of the electric discharge plasma treatment equipments 20 and 21 is carried out by the seal mechanisms 52, 53, 54, and 55, and they supply the gas 90 and 91 for after treatment which changed the inside of electric discharge plasma treatment equipment 20 and 21 into the reduced pressure state by vacuum pump P at the abbreviation vacua.
[0066] The gas which is supplied from the gas supply sections 50 and 51 for processing, and exists in throughout [counterelectrode (namely, 30/40, 31/41)] forms a laminar flow between a base material 12 and 13, and it is desirable that the rate of flow is almost uniform covering the processing width of face of a base material.
[0067] Drawing 4 shows an example of the gas supply sections 50 and 51 for processing, (A) is the cross section and (B) is the A-A cross section.
[0068] While the gas inlet 56 by which the gas supply pipe G is connected to the end section of the longitudinal direction of the direct rectangle-like gas supply section 50 for processing is formed By the ability forming [preparing two loculus in a longitudinal direction, and] the 1st room of a cam plate 14 on the diagonal line of 57 so that the 1st room may counter 57 in the gas introduction direction Form the partition which becomes so narrow that it keeps away from a gas inlet 56, and the reactant gas introduced from the gas inlet 56 is turbulent-flow-ized. abbreviation equalization of the density within the partition is carried out -- making -- the rate of flow -- abbreviation -- after deflecting the direction at the same time it considers as a uniform thing, it has the structure which rectifies gas and blows off from the stoma group 15 of uniform a large number prepared near the edge of 57 the 1st room.
[0069] It is constituted so that can prepare 58 [room / 2nd], the gas which formed the slit 25 of uniform width of face near the edge, and came out of the 1st room of the stoma group 15 of 57 may turn around a diaphragm 24 in the 2nd room 58 while arranging the diaphragm 24 with which the gas which came out of the stoma group 15 is introduced and which has the uniform crevice 23 at the end, and it may become a laminar flow from a slit 25 and it may blow off to discharge space. Thereby, the flow of the gas which came out of the stoma group 15 is equalized.
[0070] In addition, as shown in drawing 3 , although the power supply which became independent to each of each electric discharge plasma treatment equipment is being used for the high-voltage pulse power supplies 10 and 11, a common power supply may be used for them.
[0071] moreover -- although the example which makes reduced pressure only the electric discharge plasma treatment equipments 20 and 21, and replaces them by the raw gas in drawing 3 was shown -- the **** rolls 80 and 81, the taking over rolls 82 and 83, and heating and cooling systems 84 and 85 -- all may be made reduced pressure and you may replace by the raw gas
[0072] Moreover, although the example which supplies base materials 12 and 13 from the separate **** rolls 80 and 81 in drawing 3 was shown, before making the **** roll common and introducing into electric discharge plasma treatment equipment, after establishing the cutting means and cutting to required width of face, you may supply so that it may stick to the opposite side of a counterelectrode (or solid dielectric), respectively.
[0073]
[Example] Hereafter, an example is hung up and this invention is explained in more detail. In addition, in the following examples, (the Heiden lab company make, the product made from semiconductor device:IXYS, and part number IXBH40N160-627G) were used as high-voltage pulse power supply sections 10 and 11.
[0074] In the equipment shown in drawing 3 , it considered as the manufacturing installation of a surface treatment article using what has the gas diffuser of the shape of a slit shown in drawing 4 as

the gas supply sections 50 and 51 for processing. In addition, both, the up electrodes 30 and 31 of electric discharge plasma treatment equipment and the lower electrodes 40 and 41 are parallel monotonous type electrodes with a width-of-face 350x length of 150mm made from SUS304, and what coated the opposite side with the aluminum-oxide coat with a thickness of 1.5mm by the spraying process was used for them.

[0075] Base materials 12 and 13 used the polyethylene-terephthalate film (the Toray Industries, Inc. make, tradename "lumiler T50") with a thickness [of 50 micrometers], and a width of face of 300mm, and they supplied it, making it stick to the solid dielectrics 60 and 61 of the up electrodes 30 and 31, and the solid dielectrics 62 and 63 of the lower electrodes 40 and 41, and making it run the upper and lower sides by 0.5 m/min continuously from two **** rolls 80 and 81.

[0076] Subsequently, after setting the inside of electric discharge plasma treatment equipment 20 and 21 to 0.1Torr(s) by vacuum pump P, the nitrogen gas containing the tetrapod ethoxy silane of 0.5 volume % and the oxygen gas of 20 volume % was supplied by both 15SLM(s) from the argon gas which contains tetrapod isopropanal POKISHICHITANETO of 0.5 volume % from the gas supply section 50 for processing, and the gas supply section 51 for processing, and it considered as abbreviation atmospheric pressure.

[0077] subsequently, between the solid dielectrics 60 and 61 of the up electrodes 30 and 31, the solid dielectric 62 of the lower electrodes 40 and 41, and 63 -- the applied voltage of 4kV, the frequency of 6kHz, and pulse-voltage wave: -- plasma treatment was performed in drawing 1 (A), 5 microsecond [of build up time], 20 microsecond [of pulse width], and charging-time-value 20 seconds

[0078] Consequently, it is TiO2 to the front face of base materials 12 and 13. A film and SiO2 The surface treatment article 14 and 15 with which the film was formed was obtained.

[0079] The refractive index of the thin film of the obtained surface treatment article 14 and 15 and thickness were measured using the ellipsomter (the MIZOJIRI OPTICAL Co., Ltd. make, form "BVA-36VW"). Furthermore, the surface treatment article 14 and 15 was arbitrarily cut to A4 edition, and the thickness homogeneity of each thin film was measured at 5mm interval using optical interference formula automatic thickness-measurement equipment (made in NANOMETO Rix Japan, form "M-5100").

[0080] Consequently, TiO2 formed in the surface treatment article 14 and 15 Films were a refractive index 2.13 and 95nm of thickness, and the thickness distribution (R) was **3%. Moreover, SiO2 Films were a refractive index 1.44 and 128nm of thickness, and the thickness distribution (R) was **3%.

[0081] Subsequently, when the reflection factor of the obtained surface treatment article 14 and 15 was measured with the spectrophotometer (the Hitachi, Ltd. make, form "U-3000%), both visible-ray average (wavelength of 400-700nm) reflection factors are 0.2%, and the acid-resisting function was sharply given compared with the polyethylene-terephthalate film (7%). Moreover, the surface treatment article 14 and 15 is 9m2/hr, and processing area became double precision when processing efficiency sticks a base material to the electrode only by the side of one side.

[0082]

[Effect of the Invention] Since it is constituted as mentioned above, it is under the pressure near the atmospheric pressure, and the manufacture method of the surface treatment article of this invention does not need excessive plant-and-equipment investment, but manufactures efficiently the surface treatment article excellent in the adhesion of a thin film and a base material, and has few sediments by plasma treatment, and ends. Therefore, it can use for manufacture of various functional films, such as an antireflection film, an optical permselective membrane, an infrared reflective film, an antistatic film, an electromagnetic wave seal film, and semiconductor-device material, using the manufacture method of this invention.

[0083] Moreover, like the former, since it is not necessary to make the continuation manufacturing installation of the cascade screen of this invention into a reduced pressure system, its large-sized exhaust is unnecessary, and since carrying in and taking out of a raw material and a product become easy, it is very useful from the point of production operation nature and the economical efficiency of a production facility.